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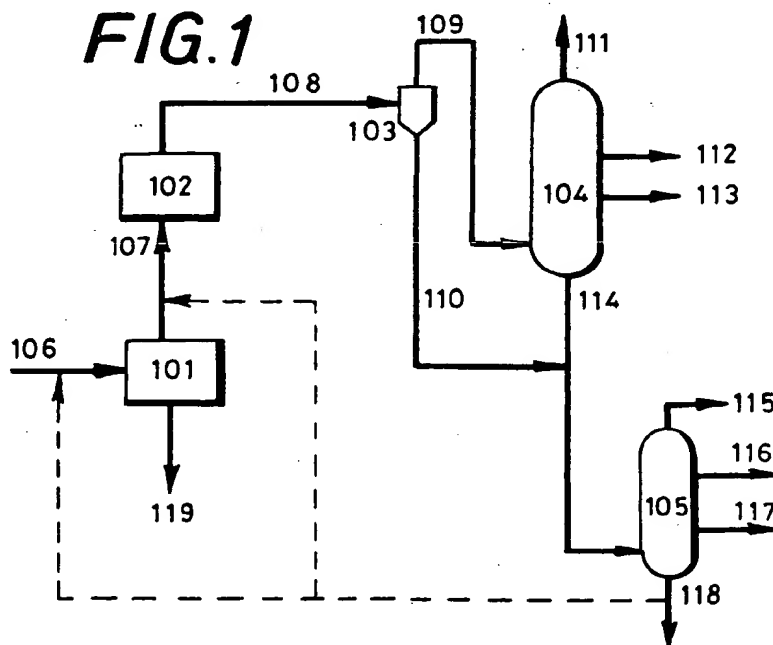
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Process for the conversion of a residual hydrocarbon oil.

- Process for the conversion of a residual hydrocarbon oil basically comprising the steps of:
- (a) deasphalting the residual hydrocarbon oil to obtain a deasphalted oil (DAO) at a yield of at least 50% by weight based on total weight of residual hydrocarbon oil and an asphaltene fraction; and
 - (b) passing part or all of the DAO through a thermal cracking zone so that a 520 °C+ conversion of at least 60% by weight based on the total weight of material boiling above 520 °C present in the DAO before thermal cracking, is obtained.



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The present invention relates to a process for the conversion of a residual hydrocarbon oil.

Thermal cracking is a widely and commonly applied route for converting residual hydrocarbon oils into lighter products. It usually involves preheating the feedstock to the appropriate temperature, thermally cracking the preheated feedstock and fractionating the effluent, which often is quenched prior to fractionation in order to stop the cracking reactions. Fractionation may for instance be conducted by atmospheric distillation solely or by a combination of atmospheric and vacuum distillation.

One of the undesired phenomena occurring in thermal cracking of residual oil feedstocks at high conversion levels is the formation of insoluble material limiting the production of distillates. This formation of insoluble material mainly originates from heavy asphaltenic components and to some extent from larger aromatic components present in the feedstocks. Additionally, insoluble material is produced from synthetic asphaltenes formed in condensation reactions occurring in the thermal cracking process. Particularly at severe cracking conditions, formation of insoluble material is known to occur. However, thermal cracking is a relatively simple process requiring a relatively low capital investment and having relatively low operating costs. This makes thermal cracking an attractive option from both a manufacturing and an economic point of view. For this reason there is a continuous effort for further improving the efficiency of thermal cracking. In the past, several methods have been proposed for achieving this goal.

In NL-A-8400074, for instance, a process for producing hydrocarbon mixtures from an oil residue is disclosed, wherein the oil residue is first deasphalted, after which the deasphalted oil is subjected to a cracking process, eventually producing one or more distillate fractions. The asphaltic bitumen fraction is partially oxidised using oxygen to produce a gasmixture containing carbon monoxide and hydrogen, which gasmixture is subsequently used in a catalytic hydrocarbon synthesis to produce synthetic hydrocarbons. These synthetic hydrocarbons are then mixed, suitably after having been separated by atmospheric distillation, with at least a part of the said distillate fractions produced in the cracking of the deasphalted oil. The cracking process, to which the deasphalted oil is subjected, most suitably is a catalytic cracking process, because the quality of the light naphtha produced by catalytic cracking is stated to be excellent. A light naphtha produced by thermal cracking, on the other hand, has to be subjected to an additional hydrogenation step for converting dienes into olefins in order to obtain a light naphtha having the desired quality.

In EP-A-0,372,652 as a disadvantage of the type of process according to NL-A-8400074 is mentioned that the asphaltenes removed from the residual oil in the deasphalting step can no longer contribute to the production of distillates and the yield of distillates is consequently not optimal. Accordingly, the process disclosed in EP-A-0,372,652 for converting a heavy hydrocarbonaceous feedstock, such as the vacuum residue of a crude oil, into lighter products involves first preheating the heavy feedstock, after which the preheated feedstock is passed through a thermal cracking zone under such conditions that a conversion of at least 35% by weight, suitably up to 70% by weight, of hydrocarbons having a boiling point of 520 °C or higher is accomplished. The effluent from the cracking zone is subsequently separated into one or more distillate fractions -to be recovered as products- and a residual fraction, which is deasphalted to obtain an asphalt and a deasphalted oil. This deasphalted oil can be further treated, e.g. by catalytic cracking, hydrotreatment, hydrocracking or thermal cracking, thus yielding more useful distillate fractions. Basically, the process disclosed involves thermal cracking under relatively severe conditions followed by deasphalting of the residual fraction. However, this process is again confronted with the fact that the asphaltenes present in the feedstock for thermal cracking limit the final yield of distillate fractions due to the formation of insoluble and/or coke material, despite the relatively severe cracking conditions. Additionally, the deasphalted oil fraction obtained from the deasphalting treatment of the thermally cracked residual oil fraction still needs further upgrading in additional conversion process units in order to attain conversion into useful distillate products.

Hence, there is still room for improvement of the efficiency of a conversion process involving thermal cracking of residual hydrocarbon oils. It is therefore an object of the present invention to provide a process for converting a residual hydrocarbon oil into lighter products of excellent quality at a high efficiency, both costwise and yieldwise. Regarding the cost-efficiency, it is an object to use as little equipment as possible without affecting the product yield and the quality of the final products. Of course, the process should also meet the appropriate safety and environmental requirements. It is a further object of the present invention to provide a process, which can be suitably integrated in various refinery configurations, such as e.g. a thermal cracker refinery, a catalytic cracker refinery, a hydrocracker refinery or a refinery which is a combination of two or more of the before-mentioned refinery configurations.

Accordingly, the present invention relates to a process for the conversion of a residual hydrocarbon oil comprising the steps of:

(a) deasphalting the residual hydrocarbon oil to obtain

(i) a deasphalted oil (DAO) at a yield of at least 50% by weight, preferably from 60 to 90% by weight, more preferably from 65 to 85% by weight, based on total weight of residual hydrocarbon oil; and
(ii) an asphaltene fraction; and

5 (b) passing part or all of the DAO through a thermal cracking zone so that a 520 °C+ conversion of at least 60% by weight, preferably from 70 to 90% by weight, based on the total weight of material boiling above 520 °C present in the DAO before thermal cracking, is obtained.

The process of the present invention thus basically involves severe thermal cracking of a deasphalted oil obtained at high yield from a residual hydrocarbon oil.

10 With the expression "520 °C+ conversion" as used throughout this specification is meant the conversion of the hydrocarbons having a boiling point of 520 °C and higher present in the thermal cracking feedstock. The 520 °C+ conversion is conveniently expressed in a weight percentage based on thermal cracking feedstock, i.e. DAO, and is determined as follows:

$$15 \quad 520 \text{ }^{\circ}\text{C+ conversion} = \frac{520 \text{ }^{\circ}\text{C+ in feed} - 520 \text{ }^{\circ}\text{C+ in effluent}}{520 \text{ }^{\circ}\text{C+ in feed}} * 100\%$$

20 It will be evident that "520 °C+" refers to the amount of hydrocarbons having a boiling point of 520 °C or higher.

An immediate advantage of the process according to the present invention is the fact that the formation of insoluble material during thermal cracking is greatly reduced due to the removal of the heavier asphaltenes from the residual hydrocarbon oil prior to thermal cracking by the deasphalting treatment. As a result, the maximum achievable conversion level is now primarily determined by the production of synthetic
25 asphaltenic components formed in condensation reactions occurring during thermal cracking instead of by the asphaltenic components present in the residual hydrocarbon oil prior to deasphalting. This implies that higher conversion levels with higher distillate productions can be achieved according to the process of the present invention than is the case with severe thermal cracking of residual oils without prior deasphalting this residual oil.

30 Another advantage of the process according to the present invention is that the quality of the distillate fractions from the thermal cracking zone is very good: the distillate fractions have an excellent H/C ratio and a low content of sulphur- and nitrogen-containing contaminants. Such contaminants, which are present in the residual hydrocarbon oil feedstock, were found to mainly concentrate in the asphalt phase produced in the deasphalting treatment rather than in the DAO. Therefore, the said contaminants, concentrated in the
35 asphalt phase, can no longer end up in the distillate fractions produced in the thermal cracking of the DAO.

Furthermore, the process has an excellent synergy potential when included in a thermal cracker refinery, a hydrocracker refinery or a catalytic cracker refinery, while incorporation in a refinery which is a combination of two or more of such refinery configurations may offer an even higher synergy potential. For the individual refinery configurations, this will be discussed and illustrated in greater detail below by figures
40 2, 3 and 4.

The residual hydrocarbon oil used as the feedstock for the process of the present invention in principle may be any residual fraction resulting from a fractionation treatment. Consequently, the residual hydrocarbon oil in any event has a relatively high content of asphaltenes. Preferably, the residual hydrocarbon oil is a heavy asphaltenes-containing hydrocarbonaceous feedstock comprising at least 35% by weight, preferably
45 at least 75% by weight and more preferably at least 90% by weight, of hydrocarbons having a boiling point of 520 °C or higher. A particularly suitable hydrocarbonaceous feedstock meeting this requirement is a vacuum residue of a crude oil, also commonly referred to as a short residue.

The deasphalting of the residual hydrocarbon oil prior to thermal cracking may be carried out in any conventional manner, such as by physical separation using membranes or by adsorption techniques.
50 However, for the purpose of the present invention it is preferred to use the well known solvent deasphalting method. In this method the residual hydrocarbon oil to be deasphalted is treated countercurrently with an extracting medium which is usually a light hydrocarbon solvent containing paraffinic compounds. Commonly applied paraffinic compounds include C₃₋₈ paraffinic hydrocarbons, suitably C₃₋₅ paraffinic hydrocarbons, such as propane, butane, isobutane, pentane, isopentane or mixtures of two or more of these. For the
55 purpose of the present invention however, it is preferred that butane, pentane or a mixture thereof is used as the extracting solvent, whereby the use of pentane is most preferred. In general, the extraction depth increases at increasing number of carbon atoms of the extracting solvent. In this connection it is noted that at increasing extraction depth, the total amount of heavy hydrocarbons being extracted together with the

lighter hydrocarbons from the residual hydrocarbon oil increases as well, while the asphaltene fraction is smaller but heavier and hence more viscous. Accordingly, the extraction depth cannot be too high as this would result in a very viscous, very heavy asphaltene fraction, which can hardly be processed any further.

In the solvent deasphalting process a rotating disc contactor or a plate column can be used with the residual hydrocarbon oil entering at the top and the extracting solvent entering at the bottom. The lighter hydrocarbons with an overall paraffinic solvency behaviour present in the residual hydrocarbon oil dissolve in the extracting solvent and are withdrawn at the top of the apparatus. The asphaltenic components which are insoluble in the extracting solvent are withdrawn at the bottom of the apparatus. The conditions under which deasphalting takes place are known in the art. Suitably, deasphalting is carried out at a total extracting solvent to residual hydrocarbon oil ratio of 1.5 to 8 wt/wt, a pressure of from 1 to 50 bar and a temperature of from 40 to 230 °C. As already described hereinbefore, for the purpose of the present invention, the deasphalting of the residual hydrocarbon oil is carried out such that a DAO is obtained at an extraction depth of at least 50% by weight, preferably from 60 to 90% by weight, more preferably 65 to 85% by weight, the balance up to 100% by weight being formed by the asphalt fraction. The expression "extraction depth" indicates the yield of DAO after deasphalting by solvent extraction and is expressed in a weight percentage based on total weight of the initial residual hydrocarbon oil prior to deasphalting.

The thermal cracking of the DAO in accordance with the present invention can be carried out by the conventional thermal cracking processes. The exact conditions under which the thermal cracking is carried out can be varied and the person skilled in the art will be able to select the temperature, the pressure and the residence time in such way that the desired conversion occurs. It will be understood that the same conversion can be obtained at a high temperature and a short residence time on the one hand and a lower temperature but longer residence time on the other hand. In order to achieve a 520 °C+ conversion of at least 60% wt on DAO, as is required in accordance with the present invention, the thermal cracking of the deasphalted oil in the thermal cracking zone is suitably conducted at a temperature of from 350 to 600 °C, a pressure of from 1 to 100 bar and average residence time of from 0.5 to 60 minutes. This residence time relates to the cold feedstock, i.e. the cold oil feedstock at ambient temperature.

The effluent from the thermal cracking zone may be quenched prior to its separation into one or more distillate fractions and a cracked residual fraction. Quenching may for instance be effected by contacting the effluent with a colder quench fluid. Suitable quench fluids include relatively light hydrocarbon oils, such as gasoline or a recycled cool residual fraction obtained from the effluent. After the optional quench, the effluent is suitably fractionated into one or more distillate fractions and a cracked residual fraction, for instance by atmospheric and/or vacuum distillation. This cracked residual fraction is rather viscous due to the presence of heavy asphaltenic components, but is considerably less viscous than the heavy asphalt phase separated from the residual hydrocarbon oil in the deasphalting step.

It is also an aspect of the present invention that the said cracked residual fraction is, in part or in total, recycled to the residual oil feedstock and/or to the DAO in order to maximise the use of plant capacity and to optimise the distillate production.

In another aspect of the present invention, the cracked residual fraction is blended with the more viscous asphalt fraction from the deasphalting treatment and the resulting blendstream is subsequently subjected to partial oxidation (gasification). The blending ratio should be adjusted such that the viscosity of the blendstream meets the viscosity specification of the gasification equipment. The production of a cracked residue, which is available as diluent for the more viscous asphalt fraction in the gasifier feedstock, offers the possibility to produce an asphalt in the deasphalting treatment with a viscosity exceeding the gasifier feedstock viscosity specification. This implies that a DAO can be produced at higher yield on residual hydrocarbon oil feed and consequently, the final production of distillates in the thermal cracking step is higher.

Gasification is suitably carried out using any well known partial oxidation process, wherein a heavy hydrocarbonaceous feedstock is partially oxidised using oxygen in the presence of steam, usually high pressure steam, thus resulting in clean gas after gas treatment. This clean gas, in return, can be applied as clean fuel gas in the refinery or for cogeneration of power and steam, hydrogen manufacture and hydrocarbon synthesis processes.

Figure 1 depicts a typical line up of the process of the present invention.

Figure 2 depicts a line up of a thermal cracking refinery.

Figure 3 depicts a line up of a catalytic cracker refinery.

Figure 4 depicts a line up of a hydrocracker refinery.

According to figure 1 residual hydrocarbon oil (106), preferably a short residue, is passed into deasphalting zone (101), resulting in a DAO (107) and an asphalt fraction (119), which is further referred to as "pentane-asphalt". The DAO (107) is led into thermal cracking zone (102), where it is heated and where

the cracking reactions take place. The reaction zone (102) may suitably consist of a furnace alone or of a combination of a furnace plus one or more soaker vessels. Upon leaving the reaction zone (102), the "cracked DAO" (108) is passed into cyclone (103), where it is quenched and separated into a cracked residue fraction (110) and a lighter fraction (109). This lighter fraction (109) is separated in atmospheric fractionator (104) into a naphtha minus fraction (111), kerosine fraction (112), gasoil fraction (113) and bottom fraction (114). This bottom fraction (114) is blended with the beforementioned cracked residue fraction (110) and the resulting blend stream is fed into vacuum distillation unit (105), where fractionation takes place into a vacuum gas oil fraction (115), a light flashed distillate (116), a heavy flashed distillate (117) and a vacuum flashed cracked residue (118). The flashed distillates (116) and (117) can be recovered as a product component or can be further upgraded, e.g. by further thermal cracking, by hydrocracking or by catalytic cracking, optionally followed by hydrotreatment. As already mentioned before, the cracked residue (118) may be partially or totally recycled to residual hydrocarbon oil feed (106) and/or to DAO (107) in order to maximise the use of plant capacity and to optimise distillate production. These options are reflected by the dotted lines in figure 1.

In figure 2 crude oil (211) is passed into atmospheric distillation unit (201) and separated into one or more distillate fractions (212), covering all fractions ranging from naphtha minus to heavy gasoil, and long residue (213). This long residue (213) is further separated in (high) vacuum distillation unit (202) in vacuum gasoil (214), light flashed distillate (215), heavy flashed distillate (216) and short residue (217). Flashed distillates (215) and (216) are combined and passed into distillate cracking unit (207). Short residue (217) is deasphalted in deasphalting zone (203), resulting in DAO (219) and pentane-asphalt (218). DAO (219) is subsequently subjected to severe thermal cracking (TC) in TC-zone (206) producing -after separation (distillation)- distillate fractions (220), which are passed into distillate cracking unit (207), and bottom product (221), which is subsequently passed into vacuum flashing unit (208) together with the bottom product (222) produced in the distillate cracking unit (207). In this vacuum flashing unit (208) separation into thermally cracked flashed distillates (223) and vacuum flashed cracked residue (224) takes place. The thermally cracked flashed distillate fraction (223) is routed to distillate cracking unit (207) and the vacuum flashed cracked residue (224) is added as a diluent to the pentane-asphalt (218), so that the resulting blendstream meets the viscosity specification of gasification unit (204). In the distillate cracking unit (207) there are further produced naphtha minus fraction (225) and gasoil fraction (226), which -after hydrodesulphurization in hydrodesulphurization unit (209)- is recovered as valuable automotive gasoil and industrial gasoil components (227). Gasification of the before-mentioned blendstream (218/224) takes place by passing this blendstream as well as oxygen (228) and steam (229) into gasification unit (204), where partial oxidation of the heavy hydrocarbons present in the said blendstream takes place to produce a gas mixture (230) mainly consisting of carbon monoxide and hydrogen, which mixture is subsequently purified in gas treatment unit (205). The purified gas (231) can be partially or totally recovered as clean fuel gas in the refinery or can be applied for the cogeneration of power and steam, hydrogen manufacture and/or hydrocarbon synthesis processes.

Compared with a thermal conversion refinery wherein the short residue is thermally cracked without prior deasphalting, the thermal conversion refinery according to figure 2 produces more distillates and less vacuum flashed cracked residue. When deasphalting the short residue at a high extraction depth by using pentane as the extracting solvent, the production of pentane-asphalt is also relatively low. The low production of both vacuum flashed cracked residue and pentane-asphalt means that less gasification capacity is required than with straight severe thermal cracking of short residues, which is attractive from both refinery margin and capital investment point of view.

In the catalytic cracker refinery according to figure 3, a crude oil (310) is separated in atmospheric distillation unit (301) into one or more distillate fractions (311), covering all fractions ranging from naphtha minus to heavy gasoil, and long residue (312), which is further separated in (high) vacuum distillation unit (302) into vacuum gasoil (313), light flashed distillate (314), heavy flashed distillate (315) and short residue (316). Short residue (316) is then deasphalted in deasphalting unit (303), resulting in pentane-asphalt (317) and DAO (318), which is passed to TC-zone (306) where thermal cracking reactions occur producing (after separation) naphtha minus (319), gasoil fraction (320) and bottom product (321). Bottom product (321) is separated in vacuum flashing unit (307) into thermally cracked flashed distillate fraction (322) and vacuum flashed cracked residue fraction (323). Thermally cracked flashed distillate fraction (322) and light and heavy flashed distillates (314) and (315) are passed into catalytic cracking zone (309), where tops (324), naphtha (325), kerosine (326), light cycle oil (327) and heavy cycle oil/clarified slurry oil (328) are produced. The light cycle oil (327) and gasoil fraction (320) are both passed through hydrodesulphurization unit (308) resulting in valuable automotive and industrial gasoil components (329). Heavy cycle oil/clarified slurry oil (328), pentane-asphalt (317) and vacuum flashed cracked residue fraction (323) are blended, so that the

resulting blendstream meets the viscosity specification of gasifier (304). The blendstream, oxygen (330) and steam (331) are passed into the gasifier (304) where the heavy hydrocarbons are partially oxidised to produce a gas mixture (332) mainly consisting of carbon monoxide and hydrogen, which gas mixture is subsequently purified in gas treatment unit (305). The purified gas (333) can be partially or totally recovered as clean fuel gas in the refinery or can be applied for the cogeneration of power and steam, hydrogen manufacture and/or hydrocarbon synthesis processes.

Compared with a long residue fluid catalytic cracker (LRFCC) refinery, a refinery with a flashed distillate fluid catalytic cracker (FDFCC) and severe thermal cracking of DAO -as illustrated by figure 3- has the advantage that no catalyst cooling capacity is required on the FDFCC, which means a significant cost saving. Additionally, contrary to an LRFCC refinery, metals present in the crude oil no longer end up on the FCC catalyst in the FDFCC refinery, thus reducing costs for FCC catalyst replacement and spent catalyst disposal or rejuvenation. Another advantage is the fact that SO_x emissions are strongly reduced in the FDFCC refinery, since the major part of the sulphur present in the long residue ends up in the pentane-asphalt after deasphalting. Sulphur removal in this case takes place in the gasifier gas treating step after partial oxidation of the gasifier feedstock mixture.

In the line up of the complex hydrocracker refinery according to figure 4 all reference numbers (401) to (433) have the same meaning as the corresponding reference numbers (201) to (233) in figure 2. The line up according to figure 4 only differs from that according to figure 2 in that flashed distillates (415) and (416) are passed into hydrocracking zone (434) instead of being passed into distillate cracking unit (407) as is the case in figure 2, where flashed distillates (215) and (216) are passed into distillate cracking unit (207). In this hydrocracking zone (434) the flashed distillates (415) and (416) are upgraded, i.e. cracked and hydrotreated, into tops (435), naphtha (436), kerosine (437), gasoil (438) and hydrowax (439). This hydrowax (439) can suitably be used as a feedstock for a chemical complex, e.g. for producing lower olefins. It is also noted that the thermally cracked flashed distillate (423) may also be partially or totally used as a feed for the hydrocracking zone (434) instead of being passed into distillate cracking zone (407).

Compared with a refinery with a hydrocracker unit (HCU) on a feedstock consisting of a mixture of flashed distillates and DAO (FD/DAO HCU), the flashed distillate hydrocracker refinery with severe thermal cracking of DAO (FD/HCU+DAO/TC refinery) according to figure 4 has the advantage that a smaller hydraulic capacity of the expensive high pressure HCU is required and that due to the absence of the DAO feed it can be operated at a lower combined feedratio, which in return results in a lower reactor volume and hence lower capital investment and operating costs. Moreover, no expensive high pressure guard bed reactor is required to protect the hydrocracker from metal contaminants and high Conradson Carbon Residue material present in the DAO feedstock. Another important advantage of the FD/HCU + DAO/TC refinery according to figure 4 is that due to the upgrading of the DAO via severe thermal cracking, the optimum DAO yield on short residue is mainly determined by the blending of the pentane-asphalt with the vacuum flashed cracked residue to meet the maximum viscosity specification of the gasifier feedstock. This optimum DAO yield is higher than the optimum DAO yield on short residue in the case of the FD/DAO HCU, the latter being predominantly determined by the maximum guard bed reactor Conradson Carbon Residue specification. Therefore, with the HCU refinery including the severe thermal cracking of DAO more DAO is available for upgrading into valuable distillates, resulting in a lower asphalt production, a lower capacity requirement for the gasifier unit and hence lower capital investment and operating costs.

The invention is further illustrated by the following examples.

Example 1

Arabian Heavy Short Residue (AHSR) was deasphalted using pentane as the extracting solvent, yielding 70% by weight on AHSR of DAO (AHSR C5-DAO). The extraction was carried out at a total solvent/feed ratio of 2.0 (wt/wt) and a feedstock predilution of 0.5 (wt/wt) at 193 °C and 40 bar pressure. The AHSR C5-DAO was subsequently subjected to severe thermal cracking at a pressure of 5.0 bar and at outlet temperatures of 470, 480, 490 and 500 °C.

Comparative Example 1

The same AHSR as used in Example 1 was subjected to thermal cracking at a pressure of 5.0 bar. Outlet temperatures were 460, 465, 470, 475 and 481 °C.

The analytical data regarding AHSR C5-DAO and AHSR are listed in Table I. The following abbreviations are used: "%w" means percent by weight and "CSt" means centistokes.

The results of the thermal cracking of AHSR C5-DAO and AHSR at the different outlet temperatures are listed in Tables II and III respectively.

TABLE I

Data regarding AHSR C5-DAO and AHSR			
		AHSR C5-DAO	AHSR
TBP/GLC			
165 - 350 °C (%w)		1.2	0
350 - 520 °C (%w)		13.3	7.0
520 °C + (%w)		85.5	93.0
Density 15/4		0.98	1.03
Viscosity	at 100 °C (CSt)	143	2351
	at 150 °C (CSt)	24	154
Sulphur (%w)		4.1	5.3
Carbon (%w)		84.4	84.0
Hydrogen (%w)		11.0	10.2
C5 asphaltenes (%w)		1.9	19.9
C7 asphaltenes (%w)		0.1	12.3
Conradson Carbon (%w)		10.2	21.7

TABLE II

Thermal cracking of AHSR C5-DAO				
Experiment No.	1	2	3	4
Outlet temp. (°C)	470	480	490	500
Product distribution:				
C4-(%w)	2.0	3.0	3.9	5.4
C5 - 165 °C (%w)	4.8	7.7	10.3	16.3
165 - 350 °C (%w)	10.0	16.5	21.2	26.6
350 - 520 °C (%w)	27.7	30.1	31.8	28.3
520 °C + (%w)	55.6	42.7	32.8	23.3
520 °C + conversion on AHSR C5-DAO (%w)	35.0	50.0	61.6	72.7
520 °C + conversion on AHSR feed (%w)	24.5	35.0	43.1	50.9
Properties of 350 °C + residual fraction:				
Density 15/4	1.01	1.01	1.03	1.04
Viscosity	at 100 °C (CSt)	79	62	51
	at 150 °C (CSt)	16	14	12
Sulphur (%w)	4.7	4.8	4.8	5.1
Carbon (%w)	84.4	84.6	84.7	84.9
Hydrogen (%w)	10.3	10.0	9.7	9.2
C5 asphaltenes (%w)	4.8	9.2	13.9	20.3
C7 asphaltenes (%w)	2.7	4.3	8.1	15.7
Conradson Carbon (%w)	11.4	13.1	15.3	18.4
Insolubles (%w)	0.01	0.01	0.01	0.03
520 °C + content (%w)	65.5	56.0	47.0	41.4

TABLE III

Thermal cracking of AHSR					
Experiment No.	1	2	3	4	5
Outlet temp. (°C)	460	465	470	475	481
Product distribution:					
C4-(%w)	2.1	2.6	3.1	2.9	3.7
C5 - 165 °C (%w)	3.7	5.1	6.1	6.7	7.5
165 - 350 °C (%w)	9.0	12.7	15.7	16.5	16.4
350 - 520 °C (%w)	21.5	22.2	22.7	22.4	22.8
520 °C+ (%w)	63.8	57.4	52.4	51.7	49.8
520 °C+ conversion on AHSR feed (%w)	31.5	38.2	43.7	44.4	46.5
Properties of 350 °C+ residual fraction:					
Density 15/4	1.05	1.06	1.01	1.07	1.08
Viscosity	at 100 °C (CSt)	1390	1376	1754	1322
	at 150 °C (CSt)	109	108	127	106
Sulphur (%w)	5.50	5.60	-	5.60	-
Carbon (%w)	84.3	83.3	84.6	84.5	84.6
Hydrogen (%w)	9.7	9.4	9.2	9.1	9.0
C5 asphaltenes (%w)	26.0	27.8	29.3	31.8	31.5
C7 asphaltenes (%w)	21.3	22.9	25.0	25.3	25.1
Conradson Carbon (%w)	20.4	28.2	28.4	28.5	29.6
Insolubles (%w)	0.13	0.52	0.39	0.54	0.48
520 °C+ content (%w)	73.9	70.2	67.5	67.7	66.3

At an insolubles content exceeding about 0.5 %w the thermal cracking pilot plant was found to block due to deposition of insoluble material. As a result, further cracking at higher conversion levels was not feasible. Using the DAO-TC route according to example 1, on the other hand, resulted in a 350 °C+ residual fraction having an insolubles content of only 0.03 %w at an outlet temperature as high as 500 °C, thus still having potential for further cracking at higher conversion levels without blocking of the pilot plant due to the deposition of insoluble material. In addition hereto, it is also evident from comparing the 520 °C+ conversion levels relative to the AHSR feed given in tables II and III, that the process according to the present invention as illustrated by example 1 allows a higher conversion and hence a higher distillate yield without blocking of the thermal cracking unit by insolubles formed.

Claims

1. Process for the conversion of a residual hydrocarbon oil comprising the steps of:

(a) deasphalting the residual hydrocarbon oil to obtain

(i) a deasphalted oil (DAO) at a yield of at least 50% by weight, preferably from 60 to 90% by weight, more preferably from 65 to 85% by weight, based on total weight of residual hydrocarbon oil; and

(ii) an asphaltene fraction; and

(b) passing part or all of the DAO through a thermal cracking zone so that a 520 °C+ conversion of at least 60% by weight, preferably from 70 to 90% by weight, based on the total weight of material boiling above 520 °C present in the DAO before thermal cracking, is obtained.

2. A process according to claim 1, wherein the residual hydrocarbon oil is a heavy asphaltenes-containing hydrocarbonaceous feedstock comprising at least 75% by weight of hydrocarbons having a boiling point of 520 °C or higher.
- 5 3. A process according to claim 2, wherein the heavy asphaltenes-containing hydrocarbonaceous feedstock is a vacuum residue of a crude oil.
4. A process according to any one of the preceding claims, wherein the deasphalting is carried out by solvent extraction using butane, pentane or a mixture thereof as the extracting solvent.
- 10 5. A process according to claim 4, wherein pentane is used as the extracting solvent.
6. A process according to any one of the preceding claims, wherein the deasphalting is carried out at a total extracting solvent to residual hydrocarbon oil ratio of 1.5 to 8 wt/wt, a pressure of from 1 to 50 bar and a temperature of from 160 to 230 °C.
- 15 7. A process according to any one of the preceding claims, wherein thermal cracking of the DAO in the thermal cracking zone is conducted at a temperature of from 350 to 600 °C, a pressure of from 1 to 100 bar and average residence time of from 0.5 to 60 minutes.
- 20 8. A process according to any one of the preceding claims, wherein the cracked residue finally obtained from the thermal cracking zone is partially or totally recycled to the residual hydrocarbon oil feed for the deasphalting treatment and/or to the DAO.
- 25 9. A process according to any one of the preceding claims, wherein at least a part of the cracked residue finally obtained from the thermal cracking zone and the asphaltene fraction from the deasphalting treatment are blended and the resulting blendstream is subsequently subjected to gasification.
- 30 10. A thermal conversion refinery wherein the process according to any one of claims 1 to 9 has been integrated.
11. A catalytic cracker refinery wherein the process according to any one of claims 1 to 9 has been integrated.
- 35 12. A hydrocracker refinery wherein the process according to any one of claims 1 to 9 has been integrated.
13. A refinery comprising a combination two or more of the refinery configurations as claimed in claims 10 to 12.

FIG. 1

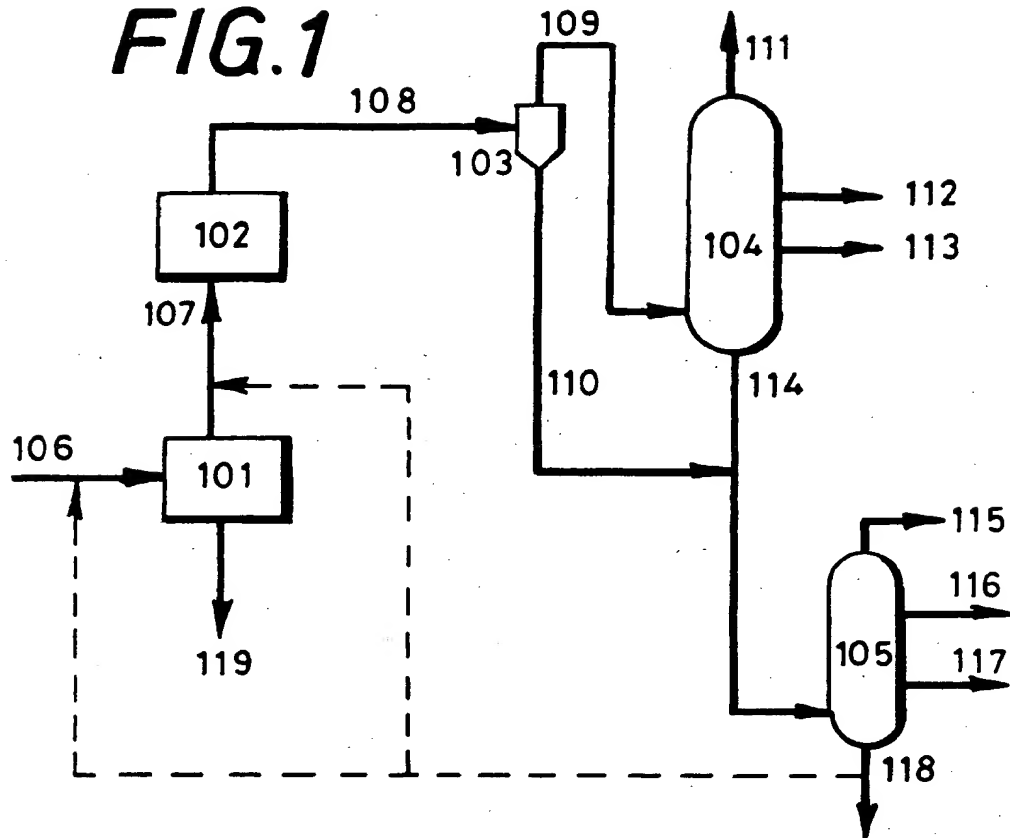
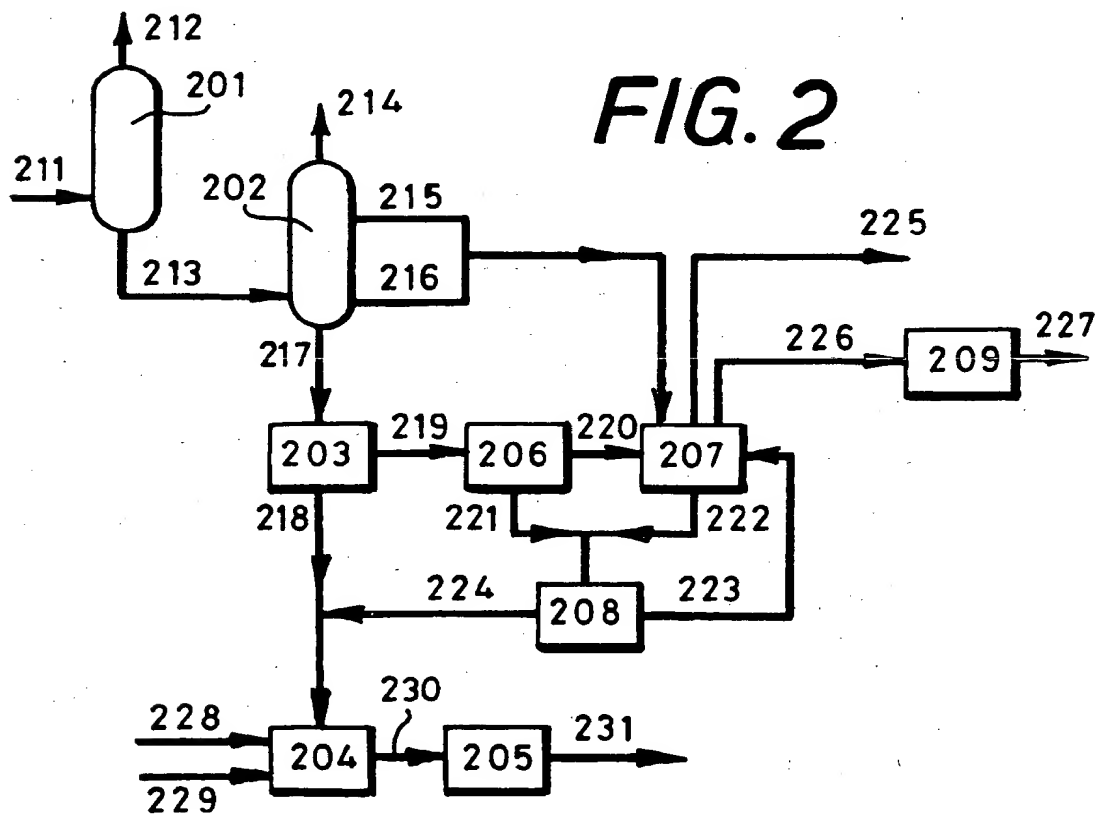
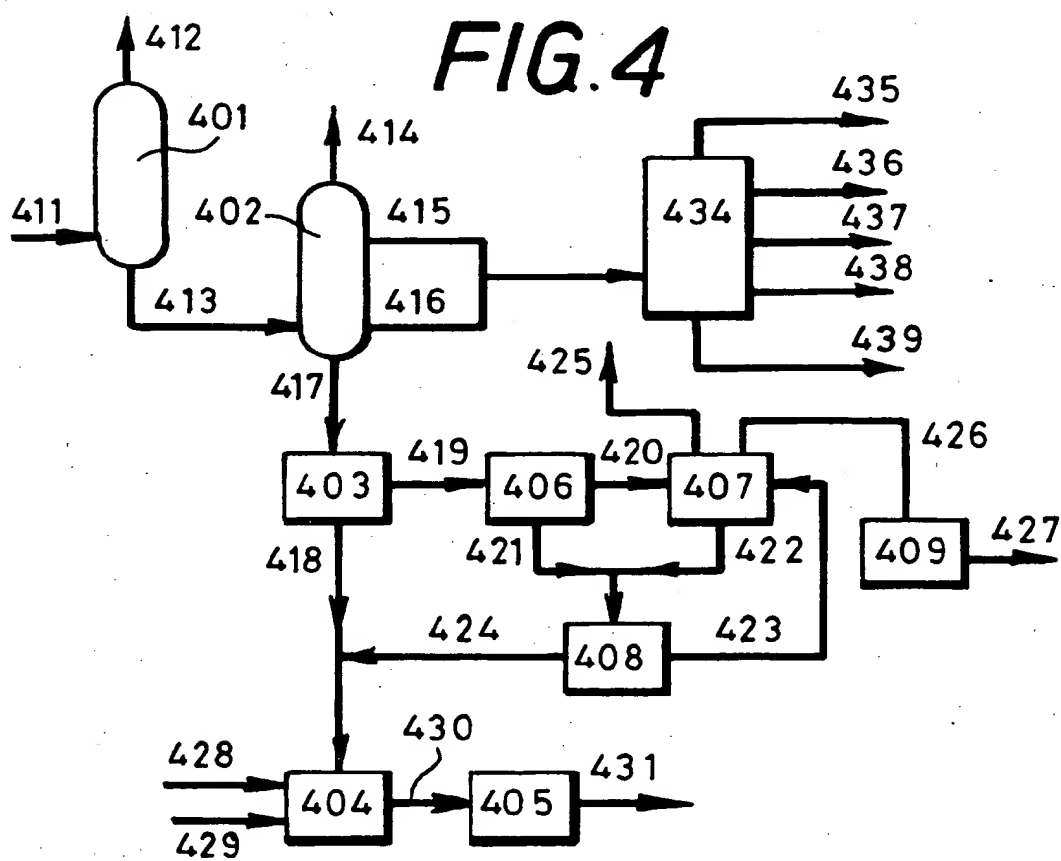
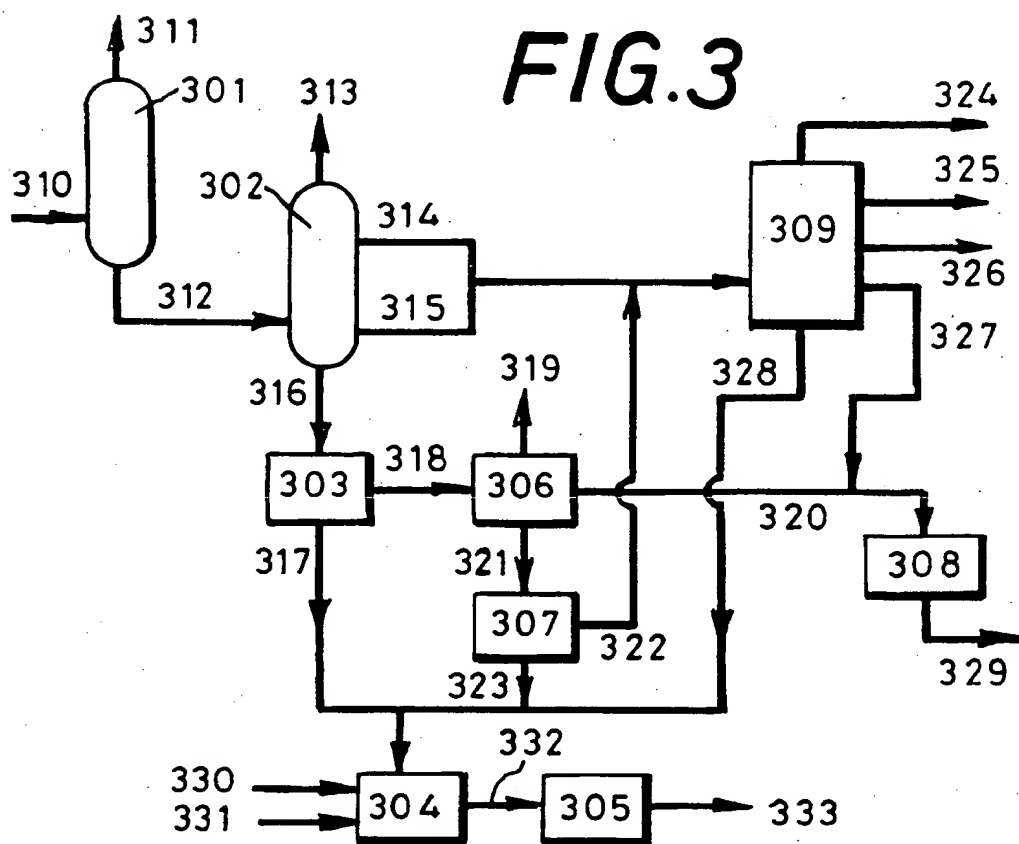


FIG. 2





(19)



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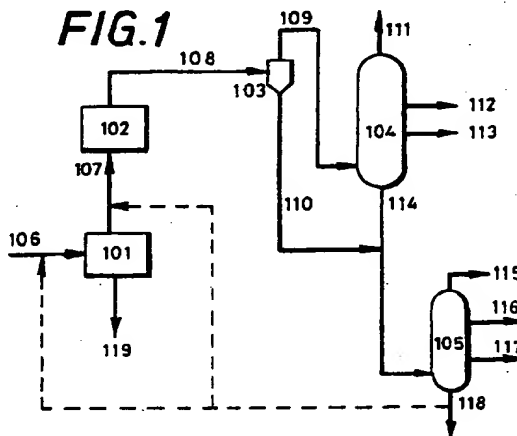
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(54) Process for the conversion of a residual hydrocarbon oil

(57) Process for the conversion of a residual hydrocarbon oil basically comprising the steps of:

- (a) deasphalting the residual hydrocarbon oil to obtain a deasphalted oil (DAO) at a yield of at least 50% by weight based on total weight of residual hydrocarbon oil and an asphaltene fraction; and
- (b) passing part or all of the DAO through a thermal cracking zone so that a 520 °C+ conversion of at least 60% by weight based on the total weight of material boiling above 520 °C present in the DAO before thermal cracking, is obtained.



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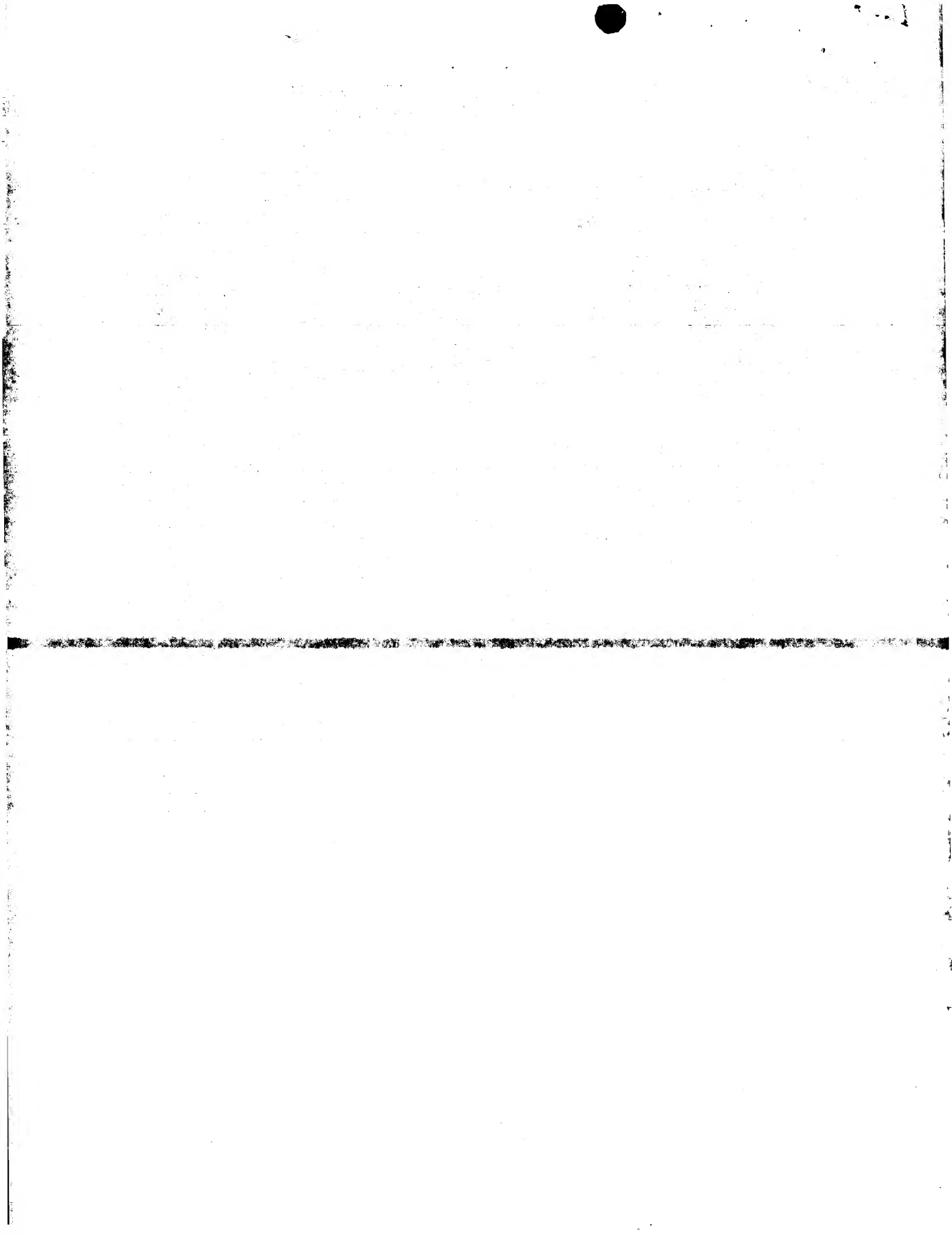
Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US-A-4 428 824 (MOBIL OIL) * the whole document *	1-13	C10G55/04
A	FR-A-2 566 795 (COMPAGNIE FRANCAISE DE RAFFINAGE) * the whole document *	1-11	
A	EP-A-0 272 577 (LUMMUS) * the whole document *	1-11	
D,A	EP-A-0 372 652 (SHELL)		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C10G
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		22 December 1995	Michiels, P
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.92 (P04C01)



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	EP 0 673 989 A (SHELL INT RESEARCH) 27 September 1995 (1995-09-27) * page 5, line 15 - line 44; claims 1,3,8,10; figure 2 * * page 4, line 26 - line 37 *	1,2,4-7	C10G55/00 C10G55/04 C10G51/02 C10G69/00 C10G51/06
Y	US 4 087 354 A (HESSLER NORMAN F) 2 May 1978 (1978-05-02) * figure 1 *	1,2,4-7	
A	US 4 640 762 A (WOODS H JOHN ET AL) 3 February 1987 (1987-02-03) * column 15, line 14 - line 16; claims 1,4,5; figures 1,2 *	1-10	
P,A	EP 0 984 054 A (ORMAT IND LTD) 8 March 2000 (2000-03-08) * figure 1 *	1-10	
D,A	GR 98 100 301 A (ORMAT PROCESS TECHNOLOGIES INC) 30 April 1999 (1999-04-30)	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
D,P, A	& US 5 976 361 A (BRONICKI LUCIEN Y ET AL) 2 November 1999 (1999-11-02) * figures 1A,1B *	1	C10G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 5 April 2002	Examiner Gilliquet, J-N
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	



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ON EUROPEAN PATENT APPLICATION NO.**

EP 00 12 3713

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05-04-2002

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0673989	A	27-09-1995	EP	0673989 A2	27-09-1995
			AU	688842 B2	19-03-1998
			AU	1492995 A	28-09-1995
			CA	2145060 A1	23-09-1995
			CN	1112600 A	29-11-1995
			JP	7286183 A	31-10-1995
			ZA	9502267 A	29-11-1995

US 4087354	A	02-05-1978	NONE		

US 4640762	A	03-02-1987	CA	1222471 A1	02-06-1987
			DE	3667179 D1	04-01-1990
			EP	0216448 A1	01-04-1987
			JP	62030189 A	09-02-1987
			NL	8601695 A	16-01-1987

EP 0984054	A	08-03-2000	US	6274003 B1	14-08-2001
			US	6183627 B1	06-02-2001
			AU	5754999 A	27-03-2000
			BR	9904043 A	29-08-2000
			CN	1323339 T	21-11-2001
			EP	0984054 A2	08-03-2000
			WO	0014178 A1	16-03-2000
			TR	9902131 A2	21-04-2000

GR 98100301	A	30-04-1999	US	5976361 A	02-11-1999
			BR	9803148 A	21-12-1999
			US	2001002654 A1	07-06-2001

